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(12) # EUROPEAN PATENT APPLICATION

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(54) **Preparation of formic acid by hydrolysis of methyl formate.**

(57) The invention provides a process for the preparation of formic acid by hydrolyzing methyl formate with water at high temperature and pressure in the presence of a formic acid catalyst. Methanol is also formed. The reesterification of the reaction products to methyl formate (a reaction favored by high temperatures) is minimized by flashing the reaction product at relatively low pressure and temperature and thereafter distilling the residual liquid. Thus procedure separates the methyl alcohol from the formic acid with a minimum contact time and at a low temperature which does not favor the reesterification reaction. High purity formic acid may be obtained by subjecting the bottom from the vacuum distillation of further distillation.

In a preferred embodiment of the invention, prior to the main hydrolysis, the methyl formate is partially hydrolyzed to form the small amount of formic acid needed to accelerate the main hydrolysis step. Accordingly, the necessary formic acid catalyst is formed *in situ*, thus eliminating the need to add formic acid or to recycle product formic acid.

Croydon Printing Company Ltd.

TITLE: PREPARATION OF FORMIC ACID BY HYDROLYSIS OF METHYL FORMATE

The formation of formic acid by the hydrolysis of alkyl formates is well-known in the art. The major drawback of such processes from the commercial standpoint is that the chemical equilibrium of the hydrolysis reaction does not favor the rapid formation of substantial amounts of formic acid. Even with mineral acid catalyst and high temperatures, the extended residence time necessary to reach equilibrium makes the process very complicated and expensive. Examples of such processes are shown in U.S. Patent 2,160,064 and British Patent 628,656. Though the use of the mineral acid catalyst did reduce reaction time, it created problems because of its tendency to promote the decomposition of the formic acid to carbon monoxide and water.

In recent years, the trend has been to perform the hydrolysis by using formic acid itself as the catalyst. While this overcame certain of the decomposition problems caused by the use of a strong mineral acid, the formic acid is less effective in accelerating the reaction.

To overcome this problem, U.S. Patent 3,907,884 proposed the use of a solvent system to reduce the reaction equilibrium time at temperatures from 25 to 150°C. This process, however, while it serves to increase the reaction rate, is not fully effective because the reactants during purification tend to undergo a reverse reaction, that is, the formic acid and the methyl alcohol present in high concentrations though no formic acid is added, the methyl formate is partially hydrolyzed to form sufficient formic acid to catalyze the main hydrolysis step. The partially hydrolyzed product from this preliminary step is combined with the recycled methyl formate and water so that the total feed to the main hydrolysis contains a molar excess of the methyl formate.

As already indicated, the present invention relates to the preparation of formic acid by the hydrolysis of the methyl formate in the presence of a formic acid catalyst. More specifically, the invention relates to a high pressure-high temperature continuous reaction autocatalyzed by formic acid, whereby the reaction product is processed so as to substantially eliminate the reesterification of the reaction products during purification. Reesterification is further suppressed by using a molar excess of methyl formate in the hydrolysis.

The formic acid catalyst required for the main hydrolysis can be added to the reaction zone, as by recycling product formic acid in a continuous process, but preferably is formed in a preliminary hydrolysis zone wherein methyl formate and a mixture of steam and water are introduced into a high temperature-high pressure zone. The main hydrolysis step of the instant invention is performed at a temperature 90 to 140°C. at pressures from 5 to 18 atmospheres, in the liquid phase at a methyl formate-water molar ratio of from 1.5:1 to 10:1, preferably from 2:1 to 4:1. Under these conditions the reactants are in a single phase. This eliminates the necessity of employing a solvent system as the system. In the flashing step a substantial amount of the unreacted methyl formate is vaporized and separated, i.e., at least 25%, preferably at least 50% of the total leaving the main hydrolyzer. The bottom from the distillation zone i.e. primarily water and formic acid may be further distilled for the removal of water and to obtain high purity, e.g. 85%, formic acid.

In the embodiment of the invention wherein the formic acid catalyst is generated in situ, prior to the main hydrolysis a portion of the methyl formate and a steam-water mixture is fed to a preliminary hydrolysis reactor maintained at elevated temperatures and pressure. This reactor is operated at similar conditions to the main hydrolyzer, namely, at temperatures of from 90 to 140°C. and pressures from 5 to 18 atmospheres. Generally lower pressures may be used because of the lower volatility of the reactants. The methyl formate-water molar ratio is from 0.5:1 to 3:1. Though no formic acid is added to the preliminary hydrolyzer, sufficient hydrolysis takes place to form sufficient formic acid to catalyse the main hydrolysis reaction. In this latter reaction zone, the contents from the preliminary reactor are combined with the methyl formate and water recycled from the distillation zone. This embodiment is of significant economic advantage because it eliminates the need for recycling purified formic acid or the addition of extraneous formic acid to the process. Since the preliminary hydrolyzer is an inexpensive addition to the overall process, this technique of forming

LINE NO.	METHYL FORMATE	WATER	FORMIC ACID	METHYL ALCOHOL
4	2478	1160	460	320
6	6088	62	285	372
7	10028	-	-	-
8	-	1118	-	-
TOTAL	18504	2340	745	695

The total feed to the main hydrolyzer 5 has a methyl formate/water mol ratio of 2.4:1. This reactor is maintained at a temperature of 120°C. and a pressure of about 9 atm. As will be understood by those skilled in the art, the formic acid formed in the preliminary hydrolyzer 1 serves as a catalyst for the reaction in the main hydrolyzer 5. Because of the severe conditions of temperature and pressure the hydrolysis reaction achieves 95% equilibrium in approximately 20 seconds.

The reaction product from the main hydrolyzer 5 contains 2645 parts of formic acid, 2013 parts of methyl alcohol, 16,116 parts of methyl formate and 1597 parts of water, and passes via line 9 to flash vessel 10. The latter is maintained at atmospheric pressure. In the flash vessel 10 a substantial portion of the unreacted methyl formate, namely 6088 parts, flashes off via line 6 rapidly cooling the remaining liquid. The vapor is recycled to the main hydrolyzer 5. The liquid passes via line 11 to a first distillation column 12, a glass-lined steel column packed with woven glass mats containing only sufficient volume to minimize liquids hold-up. The distillation column 12 is maintained at 400 mm Hg.

distillate temperature of 131°C. is maintained. The overhead stream, consisting essentially of water, is recycled via line 8 to the main hydrolyzer 5. The residue is removed via line 18, and consists of 2360 parts of formic acid and 417 parts of water, i.e., 85% formic acid.

90 to 140°C., the molar ratio of methyl formate and water in said preliminary hydrolyzer being from 0.5:1 to 3:1; partially hydrolyzing the methyl formate to form catalytic quantities of formic acid; passing the effluent directly to a main hydrolyzer; adding to said main hydrolyzer additional methyl formate and water so that the methyl formate-water molar ratio to the main hydrolyzer is from 1.5:1 to 10:1; maintaining said second reaction zone at a pressure of from 5 to 18 atms. and a temperature of from 90 to 140°C.; further hydrolyzing said methyl formate until equilibrium conditions are approached; separating the formic acid, methyl alcohol, unreacted methyl formate and water from said second reaction zone; and recycling of the separated unreacted methyl formate and water to said preliminary hydrolyzer.

5. A process according to Claim 4, wherein the effluent from the second reaction zone is passed to a low pressure zone, wherein a substantial amount of the unreacted methyl formate is vaporized overhead and the remaining liquid is thereby quickly cooled and wherein the liquid from said low pressure zone is subject to distillation to separate the residual methyl formate, the methyl alcohol and the product formic acid.

6. A process according to Claim 5, wherein the low pressure zone is maintained at about atmospheric pressure.

7. A process according to Claim 5 or Claim 6, wherein said distillation is effected in a vacuum distillation column.

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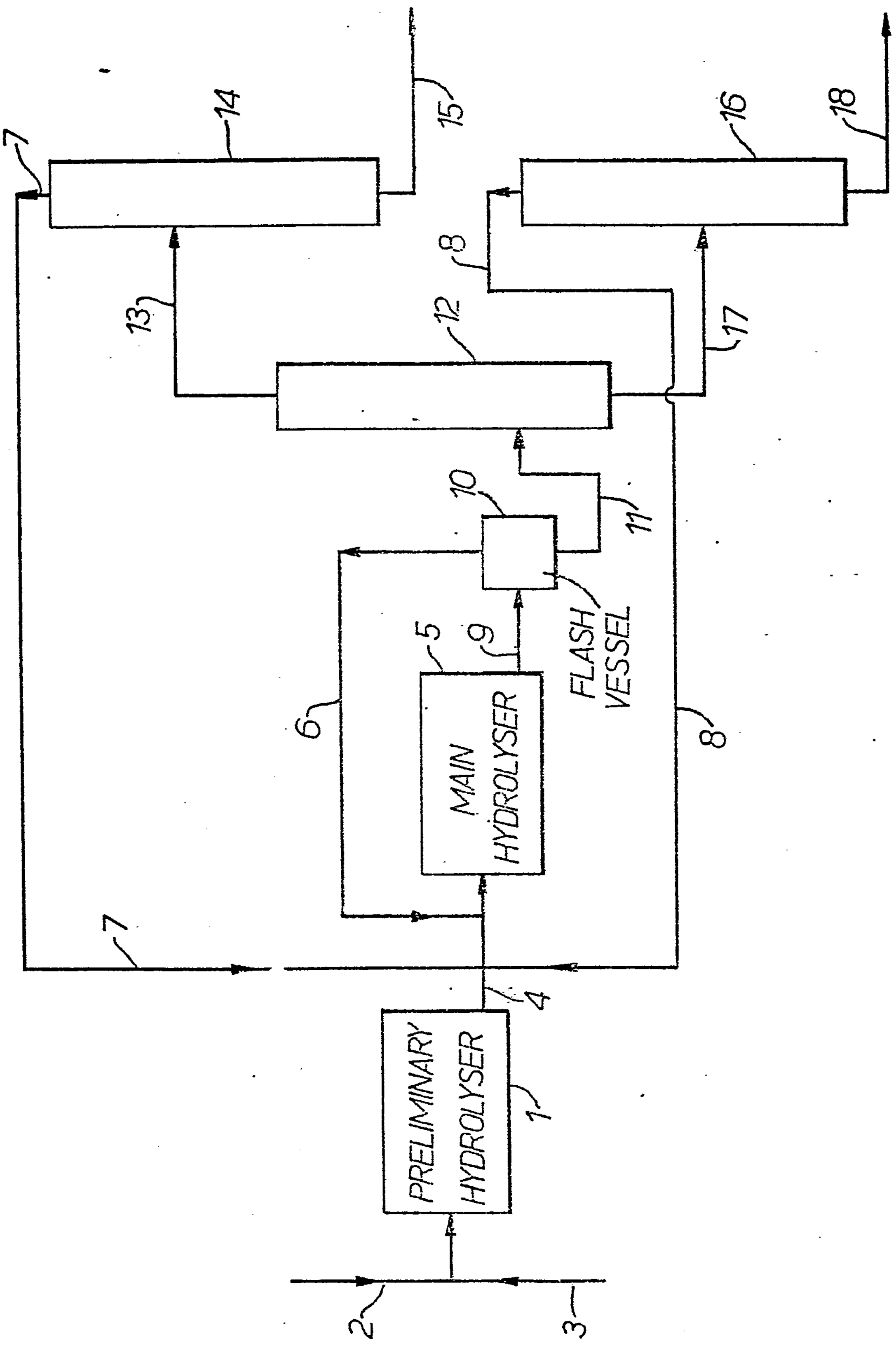
PRELIMINARY HYDROLYSER
MAIN HYDROLYSER
FLASH VESSEL
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EUROPEAN SEARCH REPORT

Application number

EP 79 300 993.7

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	DE - B - 1 035 637 (DEGUSSA) * claim 1; column 3, lines 11 to 14 * --	1, 2,6
A,D	US - A - 2 160 064 (J.F. EVERSOLE) * claim 1 * ----	1,4

CLASSIFICATION OF THE APPLICATION (Int. Cl.²)

C 07 C 53/02
C 07 C 51/09

TECHNICAL FIELDS SEARCHED (Int.Cl.²)

C 07 C 51/09
C 07 C 53/02

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

☒ The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	29-08-1979	KNAACK

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